

Claims

What Is Claimed Is:

5 1. A process for treating a metal substrate to improve adhesion of polymeric materials thereto, comprising the steps of intergranular etching a surface of the metal substrate; and applying an immersion plated metal to the intergranular etched surface by immersing the surface in an immersion plating composition comprising one or more plating metals selected from tin, silver, bismuth, copper, nickel, lead, zinc, indium, palladium, platinum, gold, cadmium, ruthenium, cobalt, gallium and germanium.

2. The process of claim 1, wherein the intergranular etched surface comprises intergranular crevices having an aspect ratio of at least about 1.

3. The process of claim 1, wherein the intergranular etched surface comprises intergranular crevices having an aspect ratio of at least about 2.

4. The process of claim 1, wherein the intergranular etched surface comprises intergranular crevices having a depth of at least about 1 micron.

5. The process of claim 1, wherein, when the intergranular etched surface is divided into a grid of squares 10 microns on each side, at least 50% of the squares include at least one intergranular crevice having an aspect ratio of at least 1.

6. The process of claim 5, wherein at least 75% of the squares include at least one intergranular crevice having an aspect ratio of at least 1.

7. The process of claim 5, wherein at least 90% of the squares include at least one intergranular crevice having an aspect ratio of at least 1.

8. The process of claim 5, wherein said at least one intergranular crevice has an aspect ratio of at least 2.

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9. The process of claim 5, wherein said at least one intergranular crevice has an aspect ratio of at least 5.

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10. The process of claim 1, further comprising a step of adhering the immersion metal plated surface to a surface of a polymeric non-conductive material.

11. The process of claim 1, wherein the steps of intergranular etching and applying the immersion plated metal are carried out in a continuous process.

12. The process of claim 1, wherein the immersion plated metal is tin.

13. The process of claim 1, further comprising a step of applying a silane over the immersion plated metal from an aqueous solution of a silane.

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14. The process of claim 13, wherein the aqueous solution of a silane comprises a solution of about 0.5 wt% to about 3 wt% of a silane selected from diethoxymethylsilylpropyltriethoxysilane, tris (triethoxysilylpropyl) amine, a trimethoxy silyl propyl modified polyethylene amine, and a mixture of γ -ureidopropyltriethoxysilane and bis(triethoxysilyl) ethane.

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15. The process of claim 13, wherein the aqueous solution of a silane has a pH in the range from about 2 to about 8.

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~~16~~. The process of claim ~~1~~, wherein the immersion plating composition further comprises a thiourea compound.

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~~17~~. The process of claim ~~16~~, wherein the immersion plating composition further comprises a urea compound.

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~~18~~. The process of claim 1, wherein the immersion plating composition comprises the at least one plating metal in the form of a salt of the metal.

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~~20~~. The process of claim 1, wherein the step of applying an immersion plated metal is carried out by passing the metal substrate through the immersion plating composition on a continuous basis .

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~~21~~. The process of claim ~~19~~, wherein the metal substrate is in contact with the immersion plating composition for a time from about 1 second to about 900 seconds.

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~~22~~. The process of claim ~~1~~, wherein the immersion plated metal has a thickness in the range from about 4 microinches to about 300 microinches.

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~~23~~. The process of claim ~~1~~, wherein the immersion plating composition comprises (a) a salt of the plating metal, (b) an acid selected from mineral acids, carboxylic acids and hydrocarbyl-substituted sulfonic acids, (c) a complexing agent and (d) water.

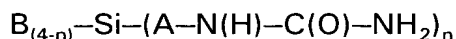
~~23~~
~~24~~. The process of claim ~~22~~, wherein (a) is a stannous salt.

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~~25~~. The process of claim ~~22~~, wherein (a) is a stannous salt of a hydrocarbyl-substituted sulfonic acid, and (b) is the hydrocarbyl-substituted sulfonic acid.

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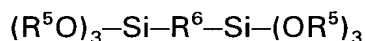
25. The process of claim 10 wherein the polymeric nonconductive material is one or more of PTFE, an epoxy resin, a polyimide, a polycyanate ester, a butadiene terephthalate resin, or mixtures thereof.

5 26. The process of claim 13 wherein the silane comprises:
(i) a ureido silane having the structure



10 wherein (A) is an alkylene group containing from 1 to about 8 carbon atoms, (B) is a hydroxy or alkoxy group containing from 1 to 8 carbon atoms, and n is an integer from 1 to 3 provided that if n is 1 or 2, each (B) may be the same or different; and

(ii) a disilyl crosslinking agent having the structure



20 wherein each R^5 is independently an alkyl group containing from 1 to about 8 carbon atoms, and R^6 is an alkylene group containing 1 to about 8 carbon atoms.

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27. The process of claim 13 wherein the silane comprises a trimethoxysilylpropyl modified polyethylene amine.

25 28. The process of claim 1, wherein the step of intergranular etching is carried out with an intergranular etching composition comprising

(a) a cupric ion source,

(b) an organic acid with an acid dissociation constant (pKa) of 5 or lower,

(c) a halide ion source, and

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(d) water.

29. The process of claim 28, wherein the cupric ion source is one or more compound(s) selected from a cupric salt of an organic acid, cupric chloride, cupric bromide and cupric hydroxide.

30. The process of claim 28, wherein the organic acid with an acid dissociation constant (pKa) of 5 or less is one or more acid(s) selected from formic acid, acetic acid, propionic acid, butyric acid, valeric acid, caproic acid, acrylic acid, crotonic acid, iso-crotonic acid, oxalic acid, malonic acid, succinic acid, glutaric acid, adipic acid, pimelic acid, maleic acid, benzoic acid, phthalic acid, cinnamic acid, glycolic acid, lactic acid, malic acid, citric acid, sulfamic acid, β -chloropropionic acid, nicotinic acid, ascorbic acid, hydroxyl pivalic acid and levulinic acid.

31. The process of claim 28, wherein the halide ion source is one or more compound(s) selected from hydrochloric acid, hydrobromic acid, sodium chloride, calcium chloride, potassium chloride, ammonium chloride, potassium bromide, copper chloride, copper bromide, zinc chloride, iron chloride, and tin bromide.

32. The process of claim 1, wherein the step of intergranular etching is carried out with an intergranular etching composition comprising
an oxidizer;
an acid;
a corrosion inhibitor; and
a source of halide ions.

33. The process of claim 32, further comprising a water soluble polymer.

34. The process of claim 33, wherein the oxidizer is selected from hydrogen peroxide and persulfates.

5 35. The process of claim 32, wherein the concentration of the oxidizer is from 6 to 60 grams per liter, the concentration of the acid is from 5 to 360 grams per liter, the concentration of the corrosion inhibitor is from 1 to 20 grams per liter and the concentration of halide ions is from 5 to 500 milligrams per liter.

10 36. The process of claim 33, wherein the corrosion inhibitor is selected from triazoles, benzotriazoles, imidazoles, benzimidazoles, tetrazoles and mixtures of the foregoing.

15 37. The process of claim 33, wherein the water soluble polymer is selected from polymers of ethylene oxide, ethylene oxide-propylene oxide copolymers, polyethylene glycols, polypropylene glycols, polyvinyl alcohols, and mixtures of the foregoing.

20 38. The process of claim 1, wherein the step of intergranular etching is carried out with an intergranular etching composition comprising 0.1 to 20% by weight hydrogen peroxide, an inorganic acid, an organic corrosion inhibitor and a surfactant.

25 39. The process of claim 38, in which the inorganic acid is selected from phosphoric acid, nitric acid, sulphuric acid, or mixtures thereof.

30 40. The process of claim 38, in which the corrosion inhibitor is selected from the group consisting of a triazole, tetrazole, and imidazole.

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41. The process of claim 38, in which the surfactant is a cationic surfactant.

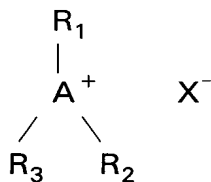
42. The process of claim 1, wherein the step of intergranular etching is carried out with an intergranular etching composition comprising

(a) hydrogen peroxide;

(b) at least one acid;

(c) at least one nitrogen-containing, five-membered heterocyclic compound which does not contain any sulphur, selenium or tellurium atom in the heterocycle; and

(d) at least one adhesive compound selected from sulfinic acids, seleninic acids, tellurinic acids, heterocyclic compounds containing at least one sulphur, selenium and/or tellurium atom in the heterocycle, and sulfonium, selenonium and telluronium salts having the general formula (A),



in which

A stands for S, Se or Te;

R₁, R₂ and R₃ stand for alkyl, substituted alkyl, alkenyl, phenyl, substituted phenyl, benzyl, cycloalkyl, substituted cycloalkyl, R₁, R₂ and R₃ being the same or different; and

X⁻ stands for an anion of an inorganic or organic acid or hydroxide, provided that the acid selected to constitute component (b) is not identical to the sulfinic, seleninic or tellurinic acids selected as component (d).

43. The process of claim 42 wherein component (c) comprises one or more triazoles, tetrazoles, imidazoles, pyrazoles and purines.

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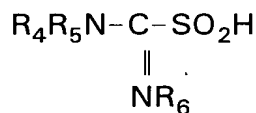
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44. The process of claim 42 wherein component (d) is a sulfinic acid selected from aromatic sulfinic acids and compounds having the formula:



wherein R_4 , R_5 and R_6 = H, alkyl, substituted alkyl, phenyl, substituted phenyl, $R_7-(CO)-$ with R_7 = H, alkyl, substituted alkyl, phenyl, substituted phenyl, wherein R_4 , R_5 and R_6 may be the same or different.

45. The process of claim 42, wherein component (d) is formamidine sulfinic acid.

46. The process of claim 42, wherein component (d) comprises one or more heterocyclic compounds selected from thiophenes, thiazoles, isothiazoles, thiadiazoles, and thiatriazoles.

47. The process of claim 42, wherein component (d) comprises one or more sulfinic acid compounds selected from benzene sulfinic acid, toluene sulfinic acid, chlorobenzene sulfinic acid, nitrobenzene sulfinic acid and carboxybenzene sulfinic acid.

48. The process of claim 42, wherein component (d) comprises one or more sulfonium salts selected from trimethyl sulfonium salts, triphenyl sulfonium salts, methioninealkyl sulfonium salts, and methionine benzylsulfonium salts.

49. The process of claim 1, wherein the step of intergranular etching is carried out with an intergranular etching composition comprising

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0.5 to 5% w/v hydrogen peroxide; and
0.01 to 5% w/v of an aromatic sulfonic acid or a salt thereof.

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50. The process of claim 49, wherein the sulfonic acid or salt thereof includes one or more aromatic groups which are carbocyclic rings.

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51. The process of claim 49, wherein the composition further comprises 0.1 to 2% w/v of a corrosion inhibitor selected from triazoles, tetrazoles, imidazoles, and mixtures thereof.

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52. The process of claim 49, wherein the sulfonic acid or salt thereof is sodium m-nitrobenzene sulfonate.

53. The process of claim 1, wherein the step of intergranular etching is carried out with an intergranular etching composition comprising:

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- (a) an acid,
 - (b) a copper complexing agent,
 - (c) a metal capable of having a multiplicity of oxidation states which is present in one of its higher positive oxidation states and which metal forms a composition soluble salt, and
 - (d) oxygen,

wherein the concentration of the higher positive oxidation state metal in the composition is greater than about 4 grams per liter of composition.

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54. The process of claim 53 wherein the metal (c) also is present in a lower positive oxidation state, and the concentration of this lower oxidation state metal is less than about 2 grams per liter of the composition.

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55. The process of claim 53 also containing copper, and the concentration of copper is less than about 2.5 grams per liter of the composition.

56. The process of claim 53 wherein the acid is a mineral acid.
57. The process of claim 53 wherein the acid is an organic acid.
58. The process of claim 53 wherein the acid is sulfuric acid.
59. The process of claim 53 wherein the metal is selected from the group consisting of tin, bismuth, lead, and cerium.
60. The process of claim 53 wherein the acid is sulfuric acid and the metal is tin.
61. The process of claim 53 wherein the copper complexing agent is a thiourea or an imidazole-thione.
62. The process of claim 53 containing greater than about 4 grams per liter of stannic ion.
63. The process of claim 62 containing less than about 2 grams per liter of stannous ion.
64. A metal substrate comprising:
an intergranular etched surface; and
an immersion plated metal layer on the intergranular etched surface.
65. The metal substrate of claim 64, wherein the intergranular etched surface includes deep intergranular crevices having an aspect ratio of at least about 1.

66. The metal substrate of claim 64, wherein the intergranular etched surface includes deep intergranular crevices having an aspect ratio of at least about 2.

67. The metal substrate of claim 64, wherein the intergranular etched surface includes deep intergranular crevices having a depth of at least about 1 micron.

68. The metal substrate of claim 64, wherein the immersion plated metal layer comprises one or more metals selected from tin, silver, bismuth, copper, nickel, lead, zinc, indium, palladium, platinum, gold, cadmium, ruthenium, cobalt, gallium and germanium.

69. The metal substrate of claim 64, further comprising a silane layer on the immersion plated metal layer.

70. The metal substrate of claim 64, wherein the silane layer comprises γ -ureidopropyltriethoxysilane and bis(triethoxysilyl)ethane.

71. The metal substrate of claim 64 wherein the silane layer comprises a trimethoxysilyl propyl modified polyethylamine.

72. The metal substrate of claim 64, wherein the immersion plated metal is tin.

73. A laminated body comprising:

- (a) a non-conductive, polymeric material; and
- (b) a metal substrate comprising:
 - a intergranular etched surface; and

an immersion plated metal layer on the intergranular etched surface.

74. The laminated body of claim 73, wherein the intergranular etched surface includes deep intergranular crevices having an aspect ratio of at least about 1.

75. The laminated body of claim 73, wherein the intergranular etched surface includes deep intergranular crevices having an aspect ratio of at least about 2.

76. The laminated body of claim 73, wherein the intergranular etched surface includes deep intergranular crevices having a depth of at least about 1 micron.

77. The laminated body of claim 73, further comprising:
(c) a silane layer on the immersion plated metal layer.

78. The laminated body of claim 73, wherein the immersion plated metal is tin.

79. The laminated body of claim 77, wherein the immersion plated metal is tin.

80. The laminated body of claim 73, wherein the polymeric material is one or more of PTFE, an epoxy resin, a polyimide, a polycyanate ester, a butadiene terephthalate resin, or mixtures thereof.

81. The laminated body of claim 77, wherein the polymeric material is one or more of PTFE, an epoxy resin, a polyimide, a polycyanate ester, a butadiene terephthalate resin, or mixtures thereof.

5 82. A metal substrate made by the process of claim 1.

83. A laminated body which comprises a metal substrate made by the process of claim 1.

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